EAST Search History

L1	302	(("5609736") or ("5843288") or ("6838065") or ("6673326") or ("6676913") or ("5814127") or ("5968334") or ("5643982") or ("6375730") or ("5749956") or ("6395144") or ("6468490") or ("6790421") or ("H001701") or ("6261525") or ("5759237") or ("5762893") or ("5779863") or ("5785741") or ("5858065") or ("5891404") or ("5919285") or ("5965786") or ("6214089") or ("6214089") or ("6254666") or ("6277173") or ("6312502") or ("6444011") or ("6558635") or ("6605133") or ("6886573") or ("6949225") or ("6023007") or ("6162957") or ("6303727") or ("6310164") or ("6362269") or ("6433102") or ("5393851") or ("5973048") or ("4290914") or ("4457904") or ("4521638") or ("4916104") or ("5321171") or ("5591238") or ("5653774") or ("5767040") or ("6177382") or ("5648549") or ("3920581") or ("4129522") or ("4243554") or ("4243553") or ("4279781") or ("4287098") or ("4320102") or ("4450098") or ("4514577") or ("4514544") or ("4814545") or ("4818350") or ("4853278") or ("4988661") or ("5023291") or ("5191137") or ("5192452") or ("5223236") or ("5302558") or ("5326903") or ("5397752") or ("5399537") or ("5399538") or ("5399749") or ("5431894") or ("5457255") or ("5463086") or ("5583081") or ("5650132") or ("5837217") or ("5849659") or ("5869013") or ("5908806") or ("5968466") or ("5980840") or ("6043186") or ("6069291") or ("6074976") or ("6146606") or ("6255506") or ("6281316") or ("6284433") or ("6319961") or ("6326432") or ("6329465") or ("6338831") or ("6344306") or ("6346253") or ("6355855") or ("6388149") or ("6399189") or ("6403031") or ("6410649") or ("6417136") or ("6420305") or ("6426438") or ("6426443") or ("6441309") or ("6458499") or ("6846471") or ("6960552") or ("4438216") or ("4337235") or ("4607112") or ("4973759") or ("5767039") or ("4260706") or	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	OFF	2006/06/23 08:10

EAST Search History

L2	0	1 and ((aluminum$1phosphorus or al$1p or (aluminum near5 phosphorus)) with ratio)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/23 08:11
L3	11	1 and (phosphorus with aluminum)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/23 08:13
L5	1	1 and (ratio same aluminum same phosphorus)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/23 08:14
L6	7	3 and ratio	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/23 08:14
S1	68360	(alumina or boehmite or pseudo$1boehmite or "aluminum trihydroxide" or "aluminum hydroxide") with catalyst	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 14:14
S2	14219	(alumina or boehmite or pseudo$1boehmite or "aluminum trihydroxide" or "aluminum hydroxide") with (phosphorus or p)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 14:00
S3	6181	S1 and S2	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:19
S4	171	(ratio with aluminum with phosphorus) and S3	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:54
S5	0	S4 and ((perfluoro$1 or fluorinated or perfluorinated) adj (compound or material))	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:21
S6	0	S4 and ((fluorinated or perfluorinated) adj (compound or material))	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:21

EAST Search History

S7	4	S4 and (fluorinated or perfluorinated)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:22
S8	1	S4 and (fluorocarbon or perfluorocarbon or "nitrogen trifluoride" or nf3 or "silicon fluoride" or "silicon hexafluoride" or sf6)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:23
S9	58	S3 and (fluorocarbon or perfluorocarbon or "nitrogen trifluoride" or nf3 or "silicon fluoride" or "silicon hexafluoride" or sf6)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:36
S10	17	"phosphorus-modified alumina"	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:29
S11	11	(ratio with aluminum with phosphorus) and S10	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:34
S12	43687	phosphorus same (phosphoric or phosphate or hydrophosphate or dihydrophosphate)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:35
S13	2591	S1 and S12	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:35
S14	235	(ratio with aluminum with phosphorus) and S13	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:35
S15	4	S14 and (fluorocarbon or perfluorocarbon or "nitrogen trifluoride" or nf3 or "silicon fluoride" or "silicon hexafluoride" or sf6)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 14:01

S16	874	(decomposing or decomposition) with (fluorocarbon or perfluorocarbon or "nitrogen trifluoride" or nf3 or "silicon fluoride" or "silicon hexafluoride" or sf6)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/23 08:08
S17	4	S13 and S16	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:38
S18	2775	(502/208,355,415).CCLS.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	OFF	2006/06/17 13:40
S19	75	(ratio with aluminum with phosphorus) and S18	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:40
S20	72	("2204157" | "2349827" | "2441297" | "2938874" | "3044954" | "3320331" | "3342750" | "3433792" | "3554926" | "3879310" | "3969273" | "4066572" | "4080311" | "4134856" | "4202798" | "4210560" | "4233184" | "4277373" | "4310440" | "4376067" | "4394525" | "4407728" | "4407730" | "4444962" | "4456780").PN. OR ("4629717").URPN.	US-PGPUB; USPAT; USOCR	OR	ON	2006/06/17 13:47
S21	61	("2301913" | "2349827" | "2365623" | "3271299" | "3320331" | "3342750" | "3904550" | "3969273").PN. OR ("4080311").URPN.	US-PGPUB; USPAT; USOCR	OR	ON	2006/06/17 13:47
S22	24	(ratio with aluminum with phosphorus) and S21	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 13:49
S23	3068	(423/323,600,625,628,629).CCLS.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	OFF	2006/06/17 13:53

EAST Search History

S24	7	(ratio with aluminum with phosphorus) and S23	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 14:06
S25	2	("4629717").PN.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	OFF	2006/06/17 13:56
S26	2	("3969273").PN.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	OFF	2006/06/17 13:57
S27	972	ratio near5 (p$1al or phosphorus$1aluminum or aluminum$1phosphorus or "aluminum to phosphorus" or "phosphorus to aluminum" or al$1p)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 14:16
S28	323	(alumina or boehmite or pseudo$1boehmite or "aluminum trihydroxide" or "aluminum hydroxide") and S27	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 14:00
S29	9	S28 and (fluorocarbon or perfluorocarbon or "nitrogen trifluoride" or nf3 or "silicon fluoride" or "silicon hexafluoride" or sf6)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 14:01
S30	132	phosphorus with modified with alumina	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 14:06
S31	29	(ratio with aluminum with phosphorus) and S30	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 14:15
S32	4839	(alumina or "aluminum oxide" or "aluminum trihydroxide") with phosphorus	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 14:13

EAST Search History

S33	619	(alumin$2 same (boehmite or pseudo$1boehmite or "aluminum trihydroxide" or "aluminum hydroxide")) and S32	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 14:15
S34	64	(ratio with aluminum with phosphorus) and S33	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 14:15
S35	28	S27 and S33	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/17 14:16
S36	14	("3284218" | "3801704" | "4324773" | "4364855" | "4459156" | "4542001" | "4833576" | "4990217" | "5496529" | "5707442" | "6022513" | "6258742").PN. OR ("6740299").URPN.	US-PGPUB; USPAT; USOCR	OR	ON	2006/06/17 14:19

EAST Search History

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	40	(588/205).CCLS.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	OFF	2006/06/23 09:34
L2	119	(588/205,206,213,258,261).CCLS.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	OFF	2006/06/23 09:34
L3	1	2 and phosphorus	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/23 09:35
L4	13	2 and aluminum	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2006/06/23 09:35

PATENT ABSTRACTS OF JAPAN

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(54) **INTERNAL COMBUSTION ENGINE EXHAUST GAS PURIFYING CATALYST AND ITS MANUFACTURE**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an internal combustion exhaust gas purifying catalyst of higher activities and temperature change stability compared with well-known catalysts.
SOLUTION: A catalyst is provided with two catalyst activity layers on a substrate, and a first layer contains several fine solids, one or more of highly dispersible alkali earth metal oxide and at least one platinum group metal, and fine solids are provided with at least one fine oxygen storage material and at least another fine component, and the platinum group metal is brought into contact closely with all the components in the first layer.

LEGAL STATUS

[Date of request for examination]	11.04.2005
[Date of sending the examiner's decision of rejection]	

* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] Some solid-states with the detailed first pass which has two catalytic activity layers on a base material, and exists on a base material, One or some high dispersibility alkaline-earth-metal oxides, and at least one platinum metal are contained. A detailed solid-state is an exhaust gas purification catalyst for internal combustion engines to which it has at least one detailed oxygen are recording ingredient and at least one another detailed component, and the platinum metal touches all the components of the first pass closely in that case.
[Claim 2] The exhaust gas purification catalyst according to claim 1 to which the platinum metal in the first pass is characterized by being platinum by palladium and the case.
[Claim 3] The second catalytic activity layer which touches exhaust gas and directly contains some detailed solid-states and at least one platinum group metals similarly. The exhaust gas purification catalyst according to claim 2 characterized by for this detailed solid-state of the second layer having at least one detailed oxygen are recording ingredient and at least one another detailed component in that case, and using a part of this detailed solid-state of the second layer as support of the platinum metal of the second layer.
[Claim 4] The exhaust gas purification catalyst according to claim 3 to which the cerium oxide on the front face of a large is used into the first pass as a detailed oxygen are recording ingredient, the mixed oxide of a cerium/zirconium is used into the second layer, the detailed component in both layers is an active calcium oxide, and the platinum metal of the second layer is characterized by being platinum by the rhodium and the case.
[Claim 5] The exhaust gas purification catalyst according to claim 4 characterized by a part of active calcium oxide of the second layer being used by a rhodium and the case as support of platinum.
[Claim 6] The exhaust gas purification catalyst according to claim 5 characterized by stabilizing the part of the active calcium oxide which the barium oxide exists as only alkaline earth metal oxide, and is used by a rhodium and the case as support of platinum into the first pass.
[Claim 7] The exhaust gas purification catalyst according to claim 2 characterized by for the first pass containing high dispersibility cerium oxide and a high dispersibility zirconium dioxide additionally, and the platinum metal of the first pass touching these components closely.
[Claim 8] The exhaust gas purification catalyst according to claim 7 to which the second catalytic activity layer is characterized by having the same structure also in claim 3.
[Claim 9] The exhaust gas purification catalyst according to claim 8 to which the mixed oxide of a cerium/zirconium is used as a detailed oxygen are recording ingredient in both layers, and an active calcium oxide is used as a detailed component, and the platinum metal of the second layer is characterized by being platinum by the rhodium and the case.
[Claim 10] The exhaust gas purification catalyst according to claim 9 characterized by a part of active calcium oxide of the second layer being used by a rhodium and the case as support of platinum.
[Claim 11] The exhaust gas purification catalyst according to claim 10 characterized by for the barium oxide existing as only alkaline earth metal oxide in the first pass, and stabilizing the parts of the active calcium oxide of the first pass, and the active calcium oxide of the second layer used by a rhodium and the case as support of platinum at least.
[Claim 12] The exhaust gas purification catalyst according to claim 11 characterized by the mixed oxide of a cerium/zirconium being stabilized by the oxidization praseodymium in both layers.

[Claim 13] The exhaust gas purification catalyst according to claim 12 characterized by for the first pass containing the mixed oxide of a zirconium/cerium detailed as an additional oxygen are recording ingredient, and the platinum metal of the first pass touching this ingredient closely in that case.
[Claim 14] The exhaust gas purification catalyst according to claim 9 characterized by the mixed oxide of the cerium/zirconium of the second layer being used by a rhodium and the case as support of platinum.
[Claim 15] The exhaust gas purification catalyst according to claim 14 characterized by the mixed oxide of the cerium/zirconium of the first pass being stabilized by the mixed oxide of the cerium/zirconium of the second layer, and the case by the oxidization praseodymium.
[Claim 16] It is an exhaust gas purification catalyst to the claim 15 publication characterized by for the barium oxide existing as only alkaline earth metal oxide in the first pass, and the active calcium oxide of the second layer being stabilized by the first pass and the case.
[Claim 17] the solid-state daily dose used as support of a platinum metal into the second layer -- an opposite -- an exhaust gas purification catalyst given [to claims 4-16 characterized by the mass ratio of the residual solid-state daily dose of the second layer being between 1:10 and 5:1] in any 1 term.
[Claim 18] The exhaust gas purification catalyst according to claim 17 characterized by the second layer containing nickel oxide as an additional detailed component by the first pass and the case.
[Claim 19] The exhaust gas purification catalyst according to claim 18 which is the inactive honeycomb object with which the base material with which both layers are prepared consists of a ceramic or a metal, and is characterized by for the amounts of covering of the first pass being per [100-300g] base material volume of 1l., and the amounts of covering of the second layer being 40-150g in that case.
[Claim 20] The exhaust gas purification catalyst according to claim 19 to which the amount of covering of the second layer is characterized by being [of the amount of covering of the first pass] only 25 - 75%.
[Claim 21] At least one detailed component in the first pass by per [base material volume of 1l. / 60-150g] concentration With the concentration whose detailed components of a detailed oxygen are recording ingredient are 20-100g, an alkaline-earth-metal oxide exists by concentration (10-40g). It exists by the concentration whose high dispersibility cerium oxide and zirconium dioxides which exist by the case are 10-70g each time. At least one detailed component in the second layer by per [base material volume of 1l. / 5-100g] concentration And the exhaust gas purification catalyst according to claim 20 characterized by existing by the concentration whose detailed components of a detailed oxygen are recording ingredient are 5-70g.
[Claim 22] The exhaust gas purification catalyst according to claim 21 characterized by for the platinum metal of the first pass existing by 0.1 - 5% of the weight of concentration to the total weight of the first pass, and the platinum metal of the second layer existing by 0.1 - 10% of the weight of concentration to the support ingredient of each time.
[Claim 23] Process which prepares aquosity covering dispersion liquid from the detailed solid-state of the following process:a first pass in the manufacture approach of an exhaust gas purification catalyst according to claim 3;
b) Process which covers a base material using these dispersion liquid, and dries and calcines an enveloping layer;
c) Process which sinks in an enveloping layer in the platinum metal of the first pass, and the water solution of the precursor compound of an alkaline-earth-metal oxide, and dries and calcines an enveloping layer;
d) Process which prepares the aquosity dispersion liquid which have the daily dose of the detailed solid-state of the second layer taken into consideration as support of the platinum metal of the second layer;
e) Process which adds the water solution of the precursor compound of the platinum metal of the second layer to the aquosity dispersion liquid of Process d;
f) Process which prepares the covering dispersion liquid of the second layer after the sorption time amount for 30 minutes at least by distributing the residual daily dose of the detailed solid-state of the second layer in the aquosity dispersion liquid of Process e;
g) The manufacture approach of the exhaust gas purification catalyst which covers with the covering dispersion liquid of Process f the base material already equipped with the first pass, and dries, and contains the process which calcines by the case.

[Claim 24] Process which adds the water solution of the precursor compound of an alkaline-earth-metal oxide, and prepares aquosity covering dispersion liquid from the detailed solid-state of the following process:a first pass in the manufacture approach of an exhaust gas purification catalyst according to claim 3;
b) Process which covers a base material with these dispersion liquid, and dries and calcines an enveloping layer;
c) Process which sinks in an enveloping layer in the water solution of the precursor compound of the platinum metal of the first pass, and dries and calcines the first pass;
d) The manufacture approach of the exhaust gas purification catalyst containing the process which manufactures a catalyst by preparing the second enveloping layer according to the processes d-g of claim 23.
[Claim 25] Process which adds the water solution of the precursor compound of the alkaline-earth-metal oxide of the first pass, and the precursor compound of a platinum metal, and prepares aquosity covering dispersion liquid from the detailed solid-state of the following process:a first pass in the manufacture approach of an exhaust gas purification catalyst according to claim 3;
b) Process which covers a base material with these dispersion liquid, and dries and calcines an enveloping layer;
c) The manufacture approach of the exhaust gas purification catalyst containing the process which manufactures a catalyst by preparing the second enveloping layer according to the processes d-g of claim 23.
[Claim 26] Process which prepares aquosity covering dispersion liquid in the manufacture approach of an exhaust gas purification catalyst according to claim 8 from the fusibility precursor compound of all the detailed solid-states and cerium oxide of the following process:a first pass, a zirconium dioxide, and an alkaline-earth-metal oxide, and the precursor compound of a platinum metal;
b) Process which covers a base material with these dispersion liquid, and dries and calcines an enveloping layer;
c) The manufacture approach of the exhaust gas purification catalyst containing the process which manufactures a catalyst by preparing the second enveloping layer according to the processes d-g of claim 23.
[Claim 27] Process which prepares aquosity covering dispersion liquid in the manufacture approach of an exhaust gas purification catalyst according to claim 8 from the fusibility precursor compound of the detailed solid-state and the cerium oxide of the following process:a first pass, a zirconium dioxide, and an alkaline-earth-metal oxide;
b) Process which covers a base material with covering dispersion liquid, and dries and calcines an enveloping layer;
c) Process which sinks in an enveloping layer in the water solution of the precursor compound of the platinum metal of the first pass, and dries and calcines an enveloping layer;
d) The manufacture approach of the exhaust gas purification catalyst containing the process which manufactures a catalyst by preparing the second enveloping layer according to the processes d-g of claim 23.
[Claim 28] Process which sinks in by the precursor compound of cerium oxide, a zirconium dioxide, and an alkaline-earth-metal oxide, and continues, and dries and calcines the detailed solid-state of the following process:a first pass in the manufacture approach of an exhaust gas purification catalyst according to claim 8;
b) Process which prepares aquosity covering dispersion liquid from the powder ingredient of Process a;
c) Process which covers a base material with these dispersion liquid, and dries and calcines an enveloping layer;
d) Process which sinks in an enveloping layer in the water solution of the precursor compound of the platinum metal of the first pass, and dries and calcines the first enveloping layer;
e) The manufacture approach of the exhaust gas purification catalyst containing the process which manufactures a catalyst by preparing the second enveloping layer according to the processes d-g of claim 23.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the exhaust gas purification catalyst for internal combustion engines which has two catalytic activity layers on a base material, and its manufacture approach.
[0002]
[Description of the Prior Art] An internal combustion engine emits a carbon monoxide CO, the nonflammable glow hydrocarbon HC, and nitrogen oxides NOx with exhaust gas as main deleterious material, and these are changed into the water, the carbon dioxide, and nitrogen which are a harmless component by the high percentage according to the latest exhaust gas purification catalyst. It is controlled so that conversion is performed on stoichiometric conditions in most, that is, the oxygen contained in exhaust gas may occur using the so-called lambda sound almost quantitatively [oxidation of a carbon monoxide and a hydrocarbon, and the reduction to the nitrogen of nitrogen oxides]. For this reason, the developed catalyst is called a three way component catalyst.
[0003] Stoichiometric conditions exist in the excess air factor lambda of 1. An excess air factor lambda means the air/fuel ratio standardized to stoichiometric conditions. It is shown what kg air since it burns completely in 1kg of fuels, is required for air/fuel ratio. In the case of the usual gasoline engine fuel, air/fuel ratio is the values of 14.6. engine exhaust gas -- a load and a rotational frequency -- responding -- the difference of extent -- that -- it has the periodic change of a strong excess air factor. Under these conditions, for good conversion of the deleterious material component of oxidizability, when [like for example, pure cerium oxide or a cerium oxide component] it exists superfluously, oxygen is combined, and when oxygen recognizes ullage existence into exhaust gas, the oxygen are recording component again emitted for oxidation conversion of oxygen is used.
[0004] This invention relates to the catalyst enveloping layer on an inactive monolith base material and the honeycomb object which has the parallel passage to exhaust gas especially. The number of the passage per cross section is called a cel consistency. According to the requirements for application, the inactive base material which has a cel consistency between 10 and 250cm-2 is used. This is a ceramic base material which consists of cordierite, a mullite, or a similar temperature-change stability ingredient and by which extrusion molding was carried out. Alternatively, the honeycomb object which consists of a steel flake is used.
[0005] A layer is called catalytic activity when the conversion mentioned to the beginning to the harmless component of the deleterious material contained in an internal combustion engine's exhaust gas in the sense of this invention can be contacted partially at least. A carbon monoxide, nitrogen oxides, and a hydrocarbon are especially counted by deleterious material, and a hydrocarbon also includes in it the hydrocarbon which exists in the form condensed on the carbon particle of exhaust gas in that case.
[0006] A catalyst enveloping layer contains other components like the ingredient of the some noble metals mostly and the large front face of the platinum group of an element periodic system and an oxygen are recording ingredient, an accelerator, and a stabilizer as a catalytic activity component. An enveloping layer is prepared on the wall of passage by well-known coating in the bottom of use of the aquosity covering dispersion liquid containing the various components of a catalyst.
[0007] This means the powdered ingredient which has the grain size between 1 micrometer and about 50

micrometers as :a "a detailed solid-state" which can add the component of a catalyst to covering dispersion liquid in various forms. the inside of English reference -- this -- receiving -- a "bulk material" or a "granular ingredient" -- an expression is used.
[0008] b) This has the grain size of 1 micrometer or less as a "colloid solid-state." The detailed grain shape structure of a solid-state and a colloid solid-state is maintained also in the manufactured catalyst enveloping layer.
[0009] c) In the form of fusibility "a precursor compound", a precursor compound is usually ****(ed) as a solid-state on the front face of a large, and it is changed into an original catalysis promotion component by heat treatment in oxidation or a reducing atmosphere, and exist in the form of high dispersibility where it has the magnitude of microcrystal 10nm or less mostly. In very high concentration or very low solubility, a precursor can exist also between detailed solid-states and can have a grain size similar to this solid-state.
[0010] The detailed solid-state of covering dispersion liquid is used as a support ingredient of the high dispersibility ingredient with which a part is obtained from a precursor compound. A detailed solid-state must have a specific surface area high for this purpose. With a large front face, the ingredient which has the specific surface area more than 10m2/g (called BET surface area) corresponds within the limits of this invention. Specific surface area can be measured using nitrogen adsorption isotherm by DIN66132.
[0011] The example of the solid-state on the front face of a large is the so-called active calcium oxide. This is a detailed aluminum oxide which has the crystal structure of the seral stage of an aluminum oxide. chi-, delta-, gamma-, kappa-, zeta-, and eta-aluminum oxide belongs to this.
[0012] An active calcium oxide has the specific surface area to 400m2/g. With the rise of temperature, the described crystal structure is mutually changed into coincidence under reduction in specific surface area (Ullmann's Encyclopedia of Industrial Chemistry; refer to the 5th edition, and 1985;aluminum volume; 557-563 pages). Above 1150 degrees C, only alpha-aluminum oxide with little surface area is stable. this process -- alkaline earth metal oxide -- especially -- the barium oxide and rare earth oxide -- it can be preferably made late with stabilization with a lanthanum trioxide or a silicon dioxide. For this reason, the stable active calcium oxide usually contains 1 - 10% of the weight of the barium oxide, a lanthanum trioxide, or a silicon dioxide to the total weight of the stable ingredient.
[0013] In order to distinguish the support ingredient on the front face of a large from the inactive monolith support for covering, the support ingredient on the front face of a large is called support (Traeger) or a support ingredient (Traegermaterialien) for this support to a base material (Tragkoerper), a call, and this within the limits of this invention.
[0014] As an oxygen are recording ingredient, the mixed oxide of pure cerium oxide or a cerium, and a zirconium is often used. A mixed oxide is got by the coprecipitation of the precursor compound of both elements. the cerium which has 50 % of the weight or more of ceriums -- the zirconium which has a thick mixed oxide and 50 thick % of the weight or more of zirconiums -- a thick mixed oxide is well-known. a cerium -- a thick mixed oxide -- the following -- the mixed oxide of a cerium/zirconium, a call, and a zirconium -- a thick mixed oxide is called the mixed oxide of a zirconium/cerium.
[0015] The European Patent 0314057BNo. 1 specification has two catalytic activity layers on a base material, the first pass which appears on the base material in that case contains platinum, and the second upper layer contains palladium. In the case of both sides, an active calcium oxide is used as a support ingredient of these components. Furthermore, in addition, a layer contains the cerium oxide introduced using the cerium compound of a cerium salt and/or a solid-state. In addition, a layer can be additionally contained with mixture by using a zirconium dioxide, lanthanum oxide, neodymium oxide, an oxidization praseodymium, and nickel oxide as the independent matter. Noble metals are introduced by sinking in into a layer. Similarly, the European Patent 0314058BNo. 1 specification indicates the three way component catalyst of platinum non-** which consists of two catalytic activity layers on a base material. The first pass contains palladium and the second layer contains a rhodium. As a support ingredient, an active calcium oxide is again used in this case. According to the European Patent No. 0314057 specification, both layers contain the same accelerator and the same stabilizer by cerium oxide and the case additionally.
[0016] A U.S. Pat. No. 5057483 specification indicates the catalyst constituent which consists of two discrete layers on a monolith base material similarly. The first pass contains the stabilization aluminum oxide and the detailed cerium oxide as a support ingredient of platinum. Furthermore, since the first pass

oppresses emission of a hydrogen sulfide, it can contain the high dispersibility barium oxide and zirconium dioxide which were distributed over all layers as a detailed iron oxide, nickel oxide, and a thermostabilizer. The second layer contains an activation aluminum oxide as the mixed oxide of the cerium/zirconium by which the rhodium is ****(ed) and which acted as Mr. [coprecipitation], and a support ingredient of platinum. The mixed oxide of the zirconium/cerium which acted as Mr. [coprecipitation] contains 2 - 30 % of the weight of cerium oxide preferably.
[0017] Another two-layer three way component catalyst is indicated by the international patent/[95th] No. 35152 specification. this catalyst -- in the first pass, first at least one stabilizer is contained by the first platinum group component and the case, and a zirconium component is contained by the case with the first support ingredient, the first palladium component, and a case by at least one first rare earth metal component and the case. The second layer contains a zirconium component by the second oxygen are recording component and the case in the second support ingredient, the second platinum component, a rhodium component, and the diluted form.
[0018] The European Patent 0734757ANo. 1 specification indicates the catalytic converter which has three platinum metals, platinum, palladium, and a rhodium. A catalyst consists of two layers on a base material. Being improved, when palladium exists in a inner layer whenever [deleterious material's conversion] and platinum and a rhodium exist all over an outer layer with this European Patent specification was found out. Furthermore, whenever [conversion] improves, when the mass (inner layer foreign layer) of both layers carries out behavior like 3:1 to 1.25:1.
[0019] The increment in severity is decided to be future legal exhaust gas threshold value. The threshold value of for example, E.U. to each deleterious material which carries out current popular use and will be proposed in the future is indicated in the 1st table. Threshold value must be maintained when carrying out a MVEG-A driving cycle to cold machine starting, acceleration transit, and partial load transit.
[0020]
[Table 1]
第１表：現在のおよび将来提案される、有害物放出の限界値

有害物	限界値 *) [g/km]		
	1996/97	2000/01	2005/06
CO	2.7	2.3	1.0
HC + NO_x	0.5		
HC		0.2	0.1
NO_x		0.15	0.08

*) これらの値は、MVEG-A 走行サイクルを実施する際に維持しなければならない。

[0021] It is planned by the 1st table that the threshold value to a carbon monoxide, a hydrocarbon, and nitrogen oxides decreases to about 1/3 of the threshold value accepted by 2005 in 1996. This improvement is possible only when succeeding in raising the catalytic activity of a well-known catalyst further now. This is possible only by prudent selection of a catalyst component, and alignment between components in the high activity level of the catalyst already attained conventionally.
[0022] The increment in the temperature-change stability of catalytic activity is also because especially the important main daily doses of emission between it, that is, a MVEG-A driving cycle are emitted in [after starting / of the engine beginning] 120 seconds in a cold machine inceptive. Although it is heated by the activation temperature very quickly with the hot exhaust gas incorporated near the engine in order to decrease cold machine starting emission, starting - and the main catalyst to which the load of the peak temperature [in / in between ordinary transit operations / the catalyst inlet port to 1050 degrees C] is carried out are used.
[0023]
[Problem(s) to be Solved by the Invention] Therefore, the technical problem of this invention is offering the catalyst which has higher activity and temperature-change stability compared with a well-known catalyst. furthermore, few [this purpose] possible amount of the noble metals used -- that is, it should be advantageously attained as much as possible on the price.

[0024]
[Means for Solving the Problem] Some solid-states with that detailed first pass that this technical problem has two catalytic activity layers on a base material, and exists on a base material, One or some high dispersibility alkaline-earth-metal oxides, and at least one platinum metal are contained. In that case, a detailed solid-state has at least one a detailed oxygen are recording ingredient and the detailed component of at least one others, and a platinum metal is solved by the exhaust gas purification catalyst which touches all the components of the first pass closely.
[0025] In the catalyst by this invention, a platinum metal forms an original catalytic activity component. Platinum, palladium, a rhodium, an osmium, and iridium belong to a platinum metal. These exist by the high distributed type which has the grain size of 10nm or less mostly in a catalyst. The relation of the concept of a platinum metal and each platinum metal itself includes all the catalytic activity appearance forms of these metals within the limits of this invention. This is whenever [higher oxidation / of these metals] besides a metal condition. Preferably, platinum is used by palladium and the case into the first pass of a catalyst.
[0026] The second catalytic activity layer of the catalyst which touches exhaust gas directly may be variously constituted according to the desired catalyst function. It is proved that the layer structure of the second layer which contains some detailed solid-states and at least one platinum metal like the first pass is advantageous in order to obtain a good three way component catalyst. In that case, this detailed solid-state of the second layer has at least one detailed oxygen are recording ingredient and the detailed component of at least one others, and some of these detailed solid-states of the second layer are used as support of the platinum metal of the second layer.
[0027] Within the limits of this invention, between "a detailed component" and "detailed oxygen are recording ingredients" is distinguished. Both things are detailed solid-states. Unlike an oxygen are recording ingredient, a detailed component does not have important oxygen are recording capacity. A detailed component and a detailed detailed oxygen are recording ingredient are partially used also as a support ingredient in a catalyst. A detailed component is the oxide of the oxide of an alkaline earth metal, a scandium, an yttrium, a gallium, an indium, silicon, titanium, a zirconium, a hafnium, germanium, tin, lead, vanadium, niobium, a tantalum, chromium, molybdenum, and a tungsten. Furthermore, the carbide, the boride, silicide, and nitride of transition metals can be used. however -- desirable -- an oxide -- an active calcium oxide is used especially. Furthermore, the mixed oxide and zeolite like an aluminum silicate and a titanate (barium titanate or - aluminum) can also be used as a detailed component.
[0028] According to the current understanding of this invention, the temperature-change stability of all enveloping layers is remarkably raised by the arrangement both first pass components were indicated to be. This arrangement stands high, when the platinum metal of the first pass touches closely all the daily doses of all the detailed solid-states of all the components of this layer, i.e., layers, and high dispersibility ingredients. In order to attain this, an another means to dispel to indicate in a detail below must be cared about in the case of first pass manufacture. Furthermore, the temperature-change stability and aging resistance of all enveloping layers improve by [of a component with the detailed platinum metal in the second layer] ****(ing) only upwards in part. Then, the part which is not covered is used as an adsorbent of catalyst poison, and it deals in it. the solid-state daily dose used as support of a platinum metal into the second layer for this purpose -- an opposite -- the mass ratio of the residual solid-state daily dose of the second layer should be between 1:4 and 1:1 preferably between 1:10 and 5:1. It depends for an advantageous mass ratio on the structure of the layer of the both sides of a catalyst, a presentation, and the average presentation of exhaust gas. With the increment in the dilution of the support particle covered with the platinum metal in the second layer (reduction in a mass ratio), contact at these catalytic activity core of the exhaust gas which carries out penetration diffusion of the second layer falls. Therefore, a 1:10 [or less] mass ratio does not deserve recommendation any longer mostly. The amount of the platinum metal non-****** daily dose which can be used for adsorption of catalyst poison with the increment in a mass ratio falls against it. Therefore, the mass ratio should be kept smaller than 5:1.
[0029] The advantageous operation form of this invention is indicated by claims 4-22.
[0030] in the special operation form of this invention, the cerium oxide on the front face of a large uses it as a detailed oxygen are recording ingredient into the first pass -- having -- the inside of the second

layer -- a cerium -- the mixed oxide of thick cerium/zirconium is used. An aluminum oxide is used as a detailed component into both layers. As a platinum metal, platinum is used by palladium and the case into the first pass, and platinum is used by a rhodium and the case into the second layer. A part of active calcium oxide of the second layer is used by a rhodium and the case as support of platinum.

[0031] Into the first pass of a catalyst, it is used for stabilization of one or some high dispersibility alkaline-earth-metal oxides like magnesium oxide, the barium oxide, and a calcium oxide. However, in all the examples of this invention, the barium oxide is preferably used as an only alkaline-earth-metal oxide.

[0032] In order to secure the high temperature-change stability of the catalytic activity of the platinum which exists by the rhodium and the case, it is advantageous to use the aluminum oxide stabilized to the aluminum-oxide part used by a rhodium and the case as support of platinum at least. The remaining aluminum oxide may be stabilized similarly. All well-known stabilization components can be used for stabilization of an aluminum oxide. Preferably, the aluminum oxide stabilized with the lanthanum trioxide is used.

[0033] Another advantageous operation form of a catalyst where the mixed oxide of detailed cerium/zirconium exists instead of the cerium oxide on the front face of a large in the first pass, and cerium oxide and a zirconium dioxide exist in the first pass by high distributed type in addition additionally to high dispersibility alkaline earth metal oxide exists to the operation form of precedence. Platinum is used by palladium and the case as a platinum metal into the first pass as in a precedence implementation form, and platinum is used by a rhodium and the case into the second layer. platinum can already be set in a precedence implementation form by the rhodium and the case -- as -- some aluminum oxides of the second layer -- it **** only upwards. Stabilizing the part of the active calcium oxide of the second layer used by a rhodium and the case as support of platinum at least also here deserves recommendation. The active calcium oxide of the first pass may be stabilized similarly. The barium oxide is used as only alkaline earth metal oxide.

[0034] The mixed oxide of a cerium/zirconium can be alternatively used instead of a part of active calcium oxide as support of platinum by the rhodium and the case into the second layer to the operation form upon which it deliberated just now.

[0035] Raising the temperature stability of a catalyst further is attained when the mixed oxide of the cerium/zirconium in the catalyst bed of one side or both sides is stabilized to the thermal load at 0.1 - 10 % of the weight of oxidization praseodymiums by the Germany patent application 19714707.No. 0 specification non-opened to the public. Alternatively, the mixed oxide of a cerium/zirconium can be used as a support ingredient of platinum by the rhodium and the case instead of an active calcium oxide into the second layer. In this case, it is advantageous especially to stabilize the mixed oxide of a cerium/zirconium by the oxidization praseodymium.

[0036] the cerium which the detailed oxygen are recording ingredient used in the operation form of the catalyst by this invention dealt with until now is pure cerium oxide, or has 70% of the weight of a cerium content preferably 60 to 90% of the weight to the total weight of a mixed oxide -- it is the mixed oxide of thick cerium/zirconium. These ingredients can come to hand on commerce. This mixed oxide has the specific surface area between comparatively stable 60 and 200m2/g to a thermal load. on the other hand, the detailed zirconium which has 20% of the weight of a cerium oxide content preferably ten to 30% of the weight to the total weight of a mixed oxide alternatively or additionally -- the mixed oxide of thick zirconium/cerium can be used. Manufacture and use of this ingredient are indicated by the U.S. Pat. No. 5057483 specification already quoted, for example.

[0037] the zirconium of these last -- a thick mixed oxide -- a thermal load -- receiving -- a cerium -- although it is more stable than a thick mixed oxide, it has slighter oxygen are recording capacity. This fault can be compensated by applying this mixture in large quantities.

[0038] a cerium -- thick and a zirconium -- one thick fault of a mixed oxide is the fact that it can use only for extent restricted for oxygen are recording of cerium oxide inside a mixed oxide. The ingredient by the Germany non-opened to the public patent application 19714707.No. 0 specification offers the better availability of the cerium oxide for oxygen are recording. This is a powder-like zirconium dioxide. Cerium oxide is prepared on the front face of a powder particle. Thereby, it can use for oxygen are recording of all the cerium oxide daily doses of an ingredient.

[0039] Among the first pass, other advantageous operation forms of a catalyst consider introducing still

more detailed nickel oxide, in order to oppress hydrogen-sulfide emission in the second layer by the case.

[0040] The first pass of a catalyst is prepared on a base material by concentration with a volume [100-300g / base material volume] of 1l., and concentration with a volume [40-150g / base material volume] of 1l. is taken into consideration to the second layer. To each component of a layer, the component with detailed :first pass to which it is proved that the following density range is advantageous is a principal component of a layer, and is applied by the concentration of 60-150g/l. A detailed oxygen are recording ingredient is introduced into an enveloping layer each time by 20-100g / base material volume of 1l. For the stabilization of an enveloping layer for an alkaline-earth-metal oxide, the amount of 10 - 40 g/l is sufficient. It was proved each time to the high dispersibility ingredient, the cerium oxide, and the zirconium dioxide which exist additionally by the case that the concentration of 10 - 70 g/l is advantageous.

[0041] The second layer is more remarkably [than the first pass] thin. This layer is preferably prepared on a base material at 30 - 50% 25 - 75% of abbreviation of the amount of covering of the first pass. The detailed oxygen are recording component of the second layer is applied by the concentration of 5 - 70 g/l each time.

[0042] The platinum metal of the first pass is introduced into a layer by 0.1 - 5% of the weight of concentration to the total weight of the first pass. This is in agreement with the concentration to 15 g/l to the base material volume. The platinum metal of the second layer is preferably used by 0.1 - 5% of the weight of concentration 0.1 to 10% of the weight to the support ingredient of each time. It was the same as the inside of the catalyst which can come to hand on commerce, or the catalyst by this invention which has more nearly little noble-metals concentration was more good, or it became clear that it had the catalytic activity of equivalence at least.

[0043] The mass ratio between platinum metals is changeable within comparatively large limits. When platinum, palladium, and a rhodium were used, it was proved that the mass ratios 3:1-1:3 of a platinum pair rhodium are advantageous. However, the mass ratio of the 1:1 neighborhoods is applied preferably. Palladium is applied in large quantities in most. Preferably, the mass ratio to the platinum is within the limits of between 10:1 and 20:1. When platinum exists in a catalyst, platinum is used together with [in the second layer] a rhodium together with [it is desirable and] palladium in both layers, i.e., the first pass. When omitting platinum in a catalyst, the mass ratio between 10:1 and 1:2 can be applied between palladium and a rhodium. A mass ratio preferably smaller than 5:1 which makes possible good catalytic activity over conversion of all three sorts of deleterious material is used.

[0044] The fact that cerium oxide and a zirconium dioxide are ****(ed) by a platinum metal (it is [palladium and] platinum by the case), alkaline earth metal oxide, and the case by high distributed type on the detailed component of the first pass and a detailed oxygen are recording ingredient is important for the catalyst by this invention. Thereby, the catalytic activity and stability of a catalyst increase clearly.

[0045] It can carry out by various approaches, i.e., ****(ing) a high dispersibility solid-state on a detailed solid-state has the approach of preparing aquosity covering dispersion liquid, then covering a catalyst base material from a solid-state detailed for the time being at it. After drying and calcining an enveloping layer, it sinks in in the water solution of the precursor compound of a platinum metal and alkaline earth metal, and this enveloping layer is dried and calcined anew. On the other hand, the precursor compound of a platinum metal and an alkaline-earth-metal oxide can also already be alternatively added to the aquosity covering dispersion liquid of a detailed solid-state. Another approach adds only the precursor compound of an alkaline-earth-metal oxide to covering dispersion liquid, covers a base material, and makes it a summary to sink in an enveloping layer by the precursor compound of noble metals succeedingly for the first time.

[0046] When using additionally high dispersibility cerium oxide and a zirconium dioxide into the first pass, these oxides are prepared on the detailed solid-state of the first pass by one routing of precedence. For this reason, the precursor compound of cerium oxide, a zirconium dioxide, and an alkaline-earth-metal oxide is dissolved in water. In this solution, a detailed solid-state (a detailed component and oxygen are recording compound) is distributed. The powder which carried out preliminary calcining is used for preparation of the first catalytic activity layer, as already indicated above.

[0047] The above-mentioned description includes only the possible process of the some for first pass

manufacture of a catalyst. Other various combination of a sinking-in process, an adsorption process, and reserve calcining is possible because of manufacture of a layer. It is guaranteeing important one touching in the layer which the selected process's manufactured as closely [a platinum metal] as all the components of a layer. for this reason -- being alike -- or [that it is independent in the precursor compound of a platinum metal in the last process] -- or it is required to introduce into covering dispersion liquid or the layer already ****(ed) on the base material together with the precursor compound of other high dispersibility components which remain in addition.

[0048] The thing of the detailed component of the second layer made to **** only upwards in part is important for the second layer in platinum by the rhodium and the case. or [that this is a part of total quantity of the aluminum oxide taken into consideration to the second layer] -- or it is the amount of an oxygen are recording solid-state. It is guaranteed that noble-metals non-****************** of sufficient amount for constant exists as a catalyst poison scavenger in the second layer by this. In order to attain this, the covering dispersion liquid of the second layer are prepared using the powder which sank in with noble metals, dried [middle-] and calcined [reserve-], and manufactured separately after that the daily dose of the detailed solid-state taken into consideration as a support ingredient of platinum by the rhodium and the case in this way, and the detailed remaining solid-state. Middle desiccation and reserve calcining prepare aquosity dispersion liquid using the part of the detailed solid-state taken into consideration as a support ingredient for the time being, and when adding in the solution of the precursor compound of noble metals, they can omit them. The detailed remaining solid-state is added for the first time for covering dispersion-liquid manufacture after the latency time for at least 30 minutes when a precursor compound adsorbs on a support ingredient. The prerequisite over the advantageous operation form in price of this covering dispersion-liquid manufacture is that a support ingredient adsorbs easily and the precursor compound as which noble metals were chosen gets.

[0049] As another, all the usual precursor compounds of a platinum metal can use this limit for manufacture of the catalyst by this invention. As alkaline earth metal oxide, cerium oxide, and a precursor compound of a zirconium dioxide, acetate and a nitrate are used preferably.

[0050] An above-mentioned desiccation process and an above-mentioned calcining process are performed in air at the temperature of 120-180 degrees C (desiccation), and the temperature of 250-500 degrees C (calcining). Calcining temperature must guarantee decomposition of a precursor compound, and change for the original catalysis promotion component of that. This is the barium oxide, the cerium oxide, and the zirconium dioxide of high distributed type [case / of barium, a cerium and a zirconium]. After calcining, a part is a metal form, a platinum metal is whenever [oxidation / with a higher part], and it exists.

[0051] A catalyst is heated during operation by the temperature to 1050 degrees C. therefore, change for the original catalysis promotion component of a precursor compound -- the formation between automobilisms -- a phase (Formierungsphase) can be entrusted. In that case, desiccation and a calcining process required between catalyst manufactures fix the enveloping layer of each time on a base material before the following process, and have the technical problem which changes a water-soluble compound into an insoluble compound. Therefore, the calcining process of all or a some can be skipped by the case.

[0052] The advantageous operation form of the some for catalyst manufacture is indicated to claims 23-28.

[0053] Some embodiments of the catalyst by this invention are compared with the catalyst by the international patent/[95th] No. 35152 specification below. : which used the following raw materials in order to manufacture a catalyst -- a La/aluminum2O3:gamma-aluminum oxide and a 2 - 4-% of the weight lanthanum -- as stabilization and a lanthanum trioxide -- count;BET surface area:140m2/g; gamma-aluminum 2O3:pure gamma-aluminum-oxide; -- initial grain-size [of BET surface area of 140m 2/g;]: -- d50**15micrometer;

CeO2 : Initial grain size of cerium-oxide;BET surface-area [pure] of 100m 2/g; of quantity surface area: d50**10micrometer;

The cerium / zirconium mixed oxide which acted as Mr. [CeO2 / / ZrO2:coprecipitation]; initial grain-size:dof content:70 % of the weight;BET surface area 60m2/g;50**30micrometer of cerium oxide;

The zirconium / cerium mixed oxide which acted as Mr. [ZrO2 / / CeO2:coprecipitation]; initial grain-size:dof content:80 % of the weight;BET surface area 50m2/g;50**3micrometer of a zirconium dioxide;

CeO2 / ZrO2/Pr 6O11: Initial grain-size:dof quantity dispersibility Pr6O11;BET surface area 60m2/g;50**17micrometer on the cerium / zirconium mixed oxide which has 67 % of the weight of cerium oxide, 28 % of the weight of zirconium dioxides, and 5 % of the weight of oxidization praseodymiums;
the Ce(C2H3O2)3:acetic-acid cerium ZrO (C2H3O2) -- 2:acetic-acid zirconyl Ba(C2H3O2)2:barium acetate NiO:nickel oxide; -- initial grain-size [of BET surface area of 20m 2/g;]: -- d50**14micrometer;
support [of a catalyst]: -- cordierite; -- 62 cel / cm2 volume: -- 1.67l. dimension: -- the temperature stability of the catalytic activity of a; with a diameter of 118.4mm die-length [of 152.4mm] this catalyst is substantially influenced mutually with the compounding ratio of the component of the first pass. This discovered situation was checked by preliminary experiment. For this reason, the base material of a catalyst was covered only with the first pass of a catalyst, respectively. Only palladium was used as a platinum metal and this was introduced into the residual component of this layer with a different compounding ratio. Residual components are a stabilization aluminum oxide, a cerium / zirconium mixed oxide, nickel oxide and high dispersibility cerium oxide, a zirconium dioxide, and the barium oxide.
[0054] By preliminary experiment 1, combination by this invention was chosen, that is, palladium was closely contacted for all the residual components of this layer. In preliminary experiment 2, palladium was deposited only on the aluminum oxide, and half palladium was deposited in preliminary experiment 3 on an aluminum oxide, and a cerium / zirconium mixed oxide, respectively.
[0055] The aquosity covering dispersion liquid which contain 20 % of the weight and nickel oxide 4.3% of the weight by using the barium oxide as barium acetate were further inserted in 30% of the weight 30% of the weight to the preliminary experiment 1 aluminum oxide by using a cerium / 30 % of the weight of zirconium mixed oxides, and cerium oxide as an acetic-acid cerium, having used the zirconium dioxide as acetic-acid zirconyl. Covering dispersion liquid were ground and it homogenized carefully. The done covering dispersion liquid had the solid-state content of 34 % of the weight, and the average grain size of about 2-4 micrometers of a detailed solid-state.
[0056] It was immersed once in said covering dispersion liquid, the base material was covered, and it dried at 120 degrees C in the air for 0.5 hours, and calcined at 500 degrees C in the air for 4 hours. Support was immersed in the palladium nitrate water solution after that, covering was infiltrated, and it dried and calcined anew. After desiccation and calcining, this base material had covering concentration about 218 g/l, and had the following presentations. : La/aluminum 2O3 100 g/l CeO2/ZrO2 30 g/l CeO ex acetate 30 g/l ZrO2 ex acetate 30 g/l BaO ex acetate 20 g/l NiO 4.3 g/l Pd The compounding ratio of many 3.8 g/l components is : [0057] which can be indicated as follows mutually.
[Formula 1]

$$\left.\begin{array}{l} La/Al_2O_3 \\ CeO_2/ZrO_2 \\ NiO \end{array}\right\} + CeO_2 + ZrO_2 + BaO + Pd$$

[0058] It differed in preliminary experiment 2 preliminary experiment 1, and before manufacturing covering dispersion liquid, palladium was beforehand fixed on the stabilization aluminum oxide. for this reason, the aluminum oxide of an initial complement -- pore space sinking in (Porenvolumenimpraegnierung) -- it sank in in the water solution of a palladium nitrate by law. done covering -- preliminary experiment 1 -- setting -- ** -- it had the same amount of covering. The compounding ratio of many components is : [0059] which can be indicated as follows mutually.
[Formula 2]

$$\left.\begin{array}{l} La/Al_2O_3 + Pd \\ CeO_2/ZrO_2 \\ NiO \end{array}\right\} + CeO_2 + ZrO_2 + BaO$$

[0060] It differed in preliminary experiment 3 preliminary experiment 1 and preliminary experiment 2, and palladium was beforehand fixed on one half, the cerium / zirconium mixed oxide, and the aluminum

oxide, respectively. done covering -- preliminary experiment 1 -- setting -- ** -- it had the same amount of covering. The compounding ratio of many components is : [0061] which can be indicated as follows.
[Formula 3]

$$\left.\begin{array}{l} La/Al_2O_3 + 0.5\ Pd \\ CeO_2/ZrO_2 + 0.5\ Pd \\ NiO \end{array}\right\} + CeO_2 + ZrO_2 + BaO$$

[0062] The rate of reaction to the deleterious material CO, HC, and NOx of the catalyst of the preliminary experiment 1-3 of 43 preliminary experiment was inspected by degradation by 1.8l. Otto engine. It deteriorated with the floor temperature (temperature of a catalyst) of 1000 degrees C in 40 hours. The rate of reaction was measured in the state of the engine trial with the floor temperature of 400 degrees C, and a different excess air factor lambda. For the simulation of actual conditions, the excess air factor was modulated by the frequency of 1Hz, amplitude**0.5 A/F (air/fuel ratio), and **1.0 A/F. The result of this measurement is indicated in the following table [2nd] and the 3rd table. Measured value given in a table is the average of at least two measurement. This table shows that combination of the component of the layer in the catalyst by this invention of preliminary experiment 1 has a clear advantage to combination of preliminary experiment 2 and 3.
[0063]
[Table 2]
第２表　1000℃で４時間のエンジン劣化後の予備実験１(VV1)、予備実験２(VV2)および予備実験３(VV3)の触媒のエンジンテスト
排気温度　400℃；排気変調：1.0 Hz ± 0.5 A/F（空気／燃料比）

予備実験	λ = 0.993			λ = 0.996			λ = 0.999			λ = 1.002			λ = 1.006		
	CO %	HC %	NO_x %	CO %	HC %	NO_x %	CO %	HC %	NO_x %	CO %	HC %	NO_x %	CO %	HC %	NO_x %
VV1	58.8	89.6	72.9	62.5	90.2	66.6	63.4	90.5	63.2	65.4	90.6	57.7	67.9	90.5	55.9
VV2	44.7	87.9	62.4	47.7	88.5	57.6	50.2	88.4	56.4	51.8	88.8	53.8	54.0	88.7	52.3
VV3	27.5	77.9	44.9	29.8	78.8	41.7	31.5	78.6	41.4	32.2	79.8	39.9	32.8	80.3	39.7

[0064]
[Table 3]
第３表　1000℃で４時間のエンジン劣化後の予備実験１(VV1)、予備実験２(VV2)および予備実験３(VV3)の触媒のエンジンテスト
排気温度　400℃；排気変調：1.0 Hz ± 1.0 A/F（空気／燃料比）

予備実験	λ = 0.993			λ = 0.996			λ = 0.999			λ = 1.002			λ = 1.006		
	CO %	HC %	NO_x %	CO %	HC %	NO_x %	CO %	HC %	NO_x %	CO %	HC %	NO_x %	CO %	HC %	NO_x %
VV1	63.1	88.4	77.3	68.4	88.5	77.3	85.3	91.3	73.9	91.7	91.4	62.8	93.7	91.4	57.7
VV2	61.9	88.5	74.5	67.0	88.6	71.7	75.7	89.6	67.0	81.6	89.7	60.0	86.3	90.1	55.4
VV3	36.7	66.3	34.8	36.2	67.1	36.1	52.3	81.8	46.1	57.7	83.7	44.9	63.9	85.7	43.4

[0065] The catalyst on the honeycomb object which has the dimension of the example above of a comparison was manufactured as given in the example of an international patent/[95th] No. 35152 specification. The :1. layer aluminum 2O3 which had the amount of covering of the following [catalyst / which was done] : 61.02 g/lNdO2 : 6.10 g/lLa 2O3 : 4.58 g/lZrO2 : 3.05 g/lSrO : 15.26 g/lZrO2/CeO2 : 30.51 g/lPd : 3.25 g/lPt : An aluminum oxide top and platinum were deposited only on the zirconium / cerium mixed oxide which has 20 % of the weight of cerium contents for palladium by the manufacture approach of a 0.07 g/l international patent/[95th] No. 35152 specification. The compounding ratio of the component of a layer is : [0066] which can be indicated as follows.
[Formula 4]

$$\left.\begin{array}{ll} Al_2O_3 & + Pd \\ ZrO_2/CeO_2 & + Pt \end{array}\right\} + NdO_2 + La_2O_3 + ZrO_2 + SrO$$

[0067]
2. Layers ZrO2/CeO2 : 73.23 g/lAl 2O3 : 30.51 g/lZrO2 : 4.58 g/lRh : 0.26 g/lPt : In the second 0.18g [/l.] layer, a rhodium and platinum were deposited only on the zirconium / cerium mixed oxide together, and this was used also in the first pass.
[0068] The compounding ratio of the component of this layer is : [0069] which can be indicated as follows.
[Formula 5]

$$\left.\begin{array}{l} Al_2O_3 \\ ZrO_2/CeO_2 + Rh + Pt \end{array}\right\} + ZrO_2$$

[0070] Total noble-metals content of this covering :P It has t+Pd+Rh=3.76 g/lPt:0.25 g/l;Pd:3.25 g/l;Rh:0.26 g/l.
[0071] Therefore, the weight ratio of a platinum metal was Pt:Pd:Rh=1:13:1.04 mutual.
[0072] It manufactured like the publication to claim 6 of the catalyst on the same honeycomb object as the example of example 1 comparison. In order to give the first pass, it consisted of an aluminum oxide and cerium oxide (quantitative ratio aluminum2O3:CeO 2= 3:2), and the aquosity covering dispersion liquid which have 55 % of the weight of solid-state contents and consistency 1.65 kg/l were manufactured. These dispersion liquid were homogenized with the mill until a solid average grain size was set to about 2-3 micrometers.
[0073] It was immersed in these dispersion liquid and the honeycomb object was covered. This covering was dried at 120 degrees C for 1 hour, and it calcined at 250 degrees C succeedingly for 2 hours. Succeedingly, it sank in with the solution which mixed a palladium nitrate and barium acetate, and this covering was dried again, and it calcined. The done first pass is :aluminum 2O3 which had the following amounts of covering. : 120 g/lCeO2 : 80 g/lBaO : 15 g/lPd : The compounding ratio of a 1.18 g/l this layer is : [0074] which can be indicated as follows.
[Formula 6]

$$\left.\begin{array}{l} Al_2O_3 \\ CeO_2 \end{array}\right\} + BaO + Pd$$

[0075] In order to manufacture the covering dispersion liquid for the second layer, the aluminum oxide which has 2.4 % of the weight of rhodiums to the aluminum oxide used first and which was stabilized with the lanthanum trioxide was inserted in. For this reason, the stabilization aluminum oxide was made to distribute underwater. The solution of a nitric-acid rhodium was added to these dispersion liquid. The cerium / zirconium mixed oxide, and the pure aluminum oxide were added to these dispersion liquid after [of sorption time amount] 30 minutes. Mutually, the amount of a stabilization aluminum oxide, a mixed oxide, and a pure aluminum oxide covered said honeycomb object with the :La/aluminum2O3:CeO2/ZrO2:aluminum2O3=1:2:2 this covering dispersion liquid which are the following ratios once again mutually, and dried and calcined. :La/aluminum 2O3 in which the second layer had the following amounts of covering : 10 g/lCeO2/ZrO2 : 20 g/lAl 2O3 : 20 g/lRh : :La/aluminum 2O3 which can indicate the compounding ratio of many components of a 0.24 g/l this layer as follows + The total noble-metals content of RhCeO2/ZrO2aluminum2O3 this covering was Pd+Rh=1.42 g/l, and were Pd:1.18 g/l, Rh:0.24 g/l, and heavy quantitative ratio Pd:Rh=5:1 at that time.
[0076] The catalyst which has a different noble-metals load like 1 2-4 examples was manufactured.
[0077]
Example 2: [ ] Pd+Rh=1.98 g/l and Pd:Rh=3:2 Example 3: Pd+Rh=2.37 g/l and Pd:Rh=1:1 Example 4: Pd+Rh=2.93 g/l and Pd:Rh=2:3 Example 5 -- being according to claim 11 -- the catalyst was manufactured like.
[0078] In order to manufacture the first pass, the water solution of an acetic-acid cerium and an acetic-acid zirconium was manufactured first. The aluminum oxide stabilized in this solution was distributed. The barium acetate solution was added succeedingly. Finally the cerium / zirconium mixed oxide was further distributed in these dispersion liquid. These dispersion liquid were dehydrated, and it dried and calcined at 500 degrees C for 2 hours.
[0079] Then, it homogenized with the mill until it distributed the obtained powder anew and a uniform

grain size of a detailed ingredient was set to 2-3 micrometers. The solution of a palladium nitrate was added to these dispersion liquid. Succeedingly, it was immersed in these dispersion liquid and the honeycomb object was covered, and it dried and calcined at 300 degrees C for 2 hours. The done layer is :La/aluminum 2O3 which had the following amounts of covering. : 100 g/lCeO2/ZrO2 : 30 g/lCeO2 : 30 g/lZrO2 : 30 g/lBaO : 20 g/lPd : The compounding ratio of many 2.51 g/l components is : [0080] which can be indicated as follows.

[Formula 7]

$$\left.\begin{array}{l} La/Al_2O_3 \\ CeO_2/ZrO_2 \end{array}\right\} + CeO_2 + ZrO_2 + BaO + Pd$$

[0081] in order to manufacture the second layer -- Example 1 -- setting -- ** -- it carried out similarly. The mixture of a nitric-acid rhodium and nitric-acid platinum was used by the weight ratio 1:1 of rhodium pair platinum instead of the pure nitric-acid rhodium. The second layer had the following amounts of covering after completion.

[0082]

La/aluminum 2O3 : 10 g/lCeO2/ZrO2 : 20 g/lAl 2O3 : 20 g/lRh : 0.16 g/lPt : :La/aluminum 2O3 which can indicate the compounding ratio of many 0.16 g/l components as follows + Total noble-metals content of Rh+PtCeO2/ZrO2aluminum2O3 this covering: It was Pt:Pd:Rh=1:16:1 at Pt+Pd+Rh=2.83 g/l and that time.

[0083] It is 850 degrees C in exhaust-gas temperature in a catalyst inlet port first, and the catalyst of the example of application 1 comparison and Examples 1-4 was degraded in the 1.8l. Otto engine over 160 hours. The deleterious material conversion rate of this catalyst was succeedingly computed through the MVEG-A-run cycle. The result is indicated in Table 4. The engine total emission is :CO:7.29g/km;HC:1.17g/km;NOx:2.88g/km which was as follows through the aforementioned run cycle without exhaust air purification.

[0084]

[Table 4]

第４表　測定された有害物変換率

触媒	Pt/Pd/Rh の比	負荷 [g/l]	コスト [%]	エミッション [g/Km] CO	HC	NO_x
VB	1/14/1	3,76	100	1,10	0,19	0,31
B1	0/5/1	1,42	40	1,42	0,23	0,45
B2	0/3/2	1,98	65	1,16	0,20	0,31
B3	0/1/1	2,37	85	1,05	0,17	0,25
B4	0/2/3	2,93	110	0,92	0,15	0,22

VB：比較例　；B1　例 1

[0085] The cost of the noble metals produced at present to what set the noble-metals load and the example of a comparison of a catalyst to 100 further in addition to the noble-metals ratio of a catalyst is indicated in the 4th table.

[0086] The 4th table shows that it has the same harmful matter conversion rate as a comparison catalyst, when the catalyst by this invention is already only 65% of the noble-metals cost of a comparison catalyst. At only 85%, the catalyst by this invention of the noble-metals cost of a comparison catalyst offers the clear more good performance data further.

[0087] The deleterious material conversion rate of the catalyst of the example of application 2 comparison and Example 5 was measured under the following test conditions by degradation of strength

床温度：　400℃

空間速度：　50000h^{-1}

空気過剰率：　λ_1＝0．998

λ_2＝1．000

λ_3＝1．002

which is different with synthesis gas equipment. :

Measurement was performed with three different excess air factors lambda1, lambda2, and lambda3.

The excess air factor was modulated by the frequency of 1Hz, and amplitude**0.8 A/F during measurement.
[0088] Two sets of catalysts are used for measurement, it is the 7-hour air at the temperature of 950 degrees C about one side of them, and another side was degraded at 1050 degrees C in the air.
[0089] The measurement result is indicated in the 5th table and the 6th table.
[0090]
[Table 5]
第５表　９５０℃で７時間の劣化後の有害物変換率

触媒	λ = 0,998			λ = 1,000			λ = 1,002		
	CO	HC	NO_x	CO	HC	NO_x	CO	HC	NO_x
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
VB	97	100	98	99	99	96	100	97	91
B1	95	99	98	97	99	97	99	99	94

[0091]
[Table 6]
第６表　１０５０℃で７時間の劣化後の有害物変換率

触媒	λ = 0,998			λ = 1,000			λ = 1,002		
	CO	HC	NO_x	CO	HC	NO_x	CO	HC	NO_x
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
VB	78	92	86	81	92	84	84	91	83
B1	89	95	96	94	95	93	95	94	87

[0092] After deteriorating at 950 degrees C, both catalysts can still be compared, as both tables show. However, after strengthening degradation with 1050 degrees C, the deleterious material conversion rate of a comparison catalyst was below the level of the catalyst by this invention substantially. In this case, better degradation stability is attained by substantial more slight noble-metals use.

[Translation done.]